# Chemical reaction at high temperature and high pressure V : kinetics of solid state reaction of zinc with phosphorus to form Zn3P2 under high pressure

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# CHEMICAL REACTION AT HIGH TEMPERATURE AND HIGH PRESSURE V

## Kinetics of Solid State Reaction of Zinc with Phosphorus to form $Zn_3P_2$ under High Pressure

BY YOSHIYUKI TANAKA*

The rate of reaction between solid powders of zinc and phosphorus to form $Zn_3P_2$ has been studied at temperatures of 50~300°C under pressures of 5~40kb. The rate was followed by measuring the amount of $Zn_3P_2$ by X-ray diffraction and found to fit the formula $1-x=6/\pi^2\sum_{n=1}^{\infty}1/n^2\exp(-n^2kt)$ which is based on the diffusion of the components into spherical particles. The kinetic data are explained on the hypothesis that the rate of reaction is determined by the diffusion of zinc followed by a slower diffusion of phosphorus. The apparent activation energy $E$ and the apparent activation volume $\Delta V^{\ddagger}$ for the diffusion process were estimated to be 14~18 kcal/mole and 3.3~4.1 cm³/mole for the temperature range 150~200°C respectively. These values are in agreement with the activation enthalpy and the activation volume of the self-diffusion of zinc given by Liu and Drickamer under high pressure.

### Introduction

The effects of pressure on the chemical reactions can be summarized as follows:

1) The equilibrium constant for the reaction may be shifted by pressure when there is an overall volume change related with the reaction.
2) The reaction should be accelerated by pressure according to the relation $\left(\frac{\partial \ln k}{\partial P}\right)_T=-\frac{\Delta V^{\ddagger}}{RT}$ when the volume of activated complex is smaller than the sum of atomic volumes of the reactants.
3) The application of pressure may radically change the products of a reaction when new paths are favored while old paths are blocked.
4) High pressure synthesis of new materials.

Besides these effects it should be also noted that high pressure generally increases effective temperature range on the chemical reactions. Pressure is sometimes required just to keep in a capsule reactants or products which may be quite volatile at the required temperature.

Owing to the advantages mentioned above, high pressure has been applied to the inorganic reactions and many investigations have been published mainly in the field of inorganic synthesis. However there are few reports discussing the reaction kinetics under high pressure. It would be ascribed to some

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difficulties in high pressure technique and interpretation of the experimental results.

Solid state physics of the materials obtained under high pressure is one of the most important fields of research in high pressure physics and chemistry. However, when describing chemical reactions, it is meaningful to speak about an activated state through which reacting species pass on their process of becoming products. Therefore it is also important physico-chemically to compile thermodynamic informations, especially apparent activation energy $E$ and apparent activation volume $\Delta V^{\ddagger}$ by studying the reaction kinetics under high pressure. The values of activation energy and activation volume not only give the temperature and pressure coefficients of the rate constant, but also suggest the state of phases of the reactants at high temperature and high pressure, if the reactions proceed through the same activated state, since the values of $E$ and $\Delta V^{\ddagger}$ depend on the enthalpy and the volumes of the reactants and those of the activated complex.

In the Zn-P system three semiconducting compounds have been well-known: tetragonal $Zn_3P_2$, tetragonal $ZnP_2$[1] and monoclinic $ZnP_2$[2]. These compounds have been prepared generally through the heterogeneous liquid-vapor reaction of molten zinc and phosphorus vapor under atmospheric pressure. The open system[1], in which phosphorus vapor is passed over the heated metallic zinc, yields the tetragonal $ZnP_2$ and $Zn_3P_2$ at 700°C. On the other hand, a sealed quartz system[2] containing enough excess phosphorus gives only the two modifications of $ZnP_2$, their ratios being controlled by the phosphorus pressure. Under atmospheric pressure the $ZnP_2$ once formed decomposes to $Zn_3P_2$ and phosphorus, and $Zn_3P_2$ also decomposes gradually to elements above 500°C[3]. There have been no report dealing with the kinetics of these reactions since the reactions do not proceed quantitatively because of the heterogeneous reactions and the decomposition of products.

In the present work the kinetics of the solid state reaction of zinc with phosphorus to form $Zn_3P_2$ has been investigated at temperatures of 100~400°C under pressures of 5~40 kb. The present investigation was also undertaken to make clear the reaction processes of zinc and phosphorus by suppressing the decompositions of products by high pressure.

In the case of Zn : P=3 : 2 starting mixture, only $Zn_3P_2$ was formed throughout the experimental conditions covered. The rate of reaction was found to fit the rate equation $1-x=6/\pi^2\sum_{n=1}^{\infty}1/n^2\exp(-n^2kt)$ which is based on the diffusion of components into spherical particles. The kinetic data are explained on the hypothesis that the rate of reaction is determined by the diffusion of zinc.

In the specimen containing excess phosphorus, on the other hand, both $Zn_3P_2$ and the monoclinic $ZnP_2$ were formed at about 500°C below 13 kb. Although the monoclinic $ZnP_2$ once formed transforms into the tetragonal $ZnP_2$ above 600°C under these conditions, a new pressure-induced polymorphic transition of monoclinic $ZnP_2$ into a pseudo-cubic form takes place in the higher pressure range above 15~20 kb. Details of the new polymorphic transition at high temperature and high pressure will be described in the following paper[4].

1) M. V. Stackelberg and R. Paulus, *Z. physik. Chem.*, **B28**, 427 (1935)
2) I. J.Hegyi, E. E. Loebner, E. W. Poor, Jr. and J. G. White, *J. Phys. Chem. Solids*, **24**, 333 (1963)
3) R. C. Schoonmaker, A. R. Venkitaraman and P. K. Lee, *J. Phys. Chem.*, **71**, 2676 (1967)
4) Y. Tanaka, *This Journal*, **38**, 151 (1968)

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## Experimentals

### Materials

Extra pure zinc and red phosphorus were obtained commercially and mixed thoroughly in the atomic ratio of Zn : P=3 : 2 in an agate mortar. Red phosphorus is amorphous and a little cohesive so that it could not be sieved. Each series of experiments was performed with portions of the same reactant mixture stored in a desiccator. An electron micrograph of the mixture showed that the particles were in the vicinity of $5\,\mu$.

### High pressure technique and analysis

A compact cubic anvil apparatus[5] was used throughout the experiments. The details of the construction of the apparatus, the pyrophyllite cubic cell geometry and resistance strip-heater arrangement have been described earlier[6]. The reactions were carried out in cylindrical glassy carbon sample holders inserted into a pyrophyllite cube without a pyrophyllite sheath. Chromel-alumel thermocouples were used for temperature measurement. The junction of the thermocouple was adjacent to the center of glassy carbon sample holder. The pressure effect on the emf of this couple was relatively small and neglected. After pressure had been applied, the temperature was elevated to the desired value. It took 1~2 minutes to reach a given temperature. After the runs, an almost instantaneous quench to room temperature from the elevated temperature was achieved by the power cut off, and then pressure was released slowly. X-ray diffraction (Ni-filtered Cu-K$\alpha$ radiation) was used to follow the reaction yield by measuring the amount of $Zn_3P_2$ produced in the reaction. The calibration curve to determine the amount of $Zn_3P_2$ was made using $CaF_2$ as an internal standard. The (224,400) peak of $Zn_3P_2$ and the (111) peak of $CaF_2$ were utilized for quantitative analysis. The specimen was pulverized and weighed, and then a certain amount of $CaF_2$ was added. After enough mixing the specimen was divided into halves and each specimen was analysed three times in order to obtain a statistical value. The six line intensities were averaged to obtain the value for the specimen. It was confirmed by the experiments that $Zn_3P_2$ was the only product for the Zn : P=3 : 2 starting mixture under any experimental conditions. Therefore, the data obtained by analyzing the amount of $Zn_3P_2$ formed actually describe the overall reaction of zinc with phosphorus to form $Zn_3P_2$.

## Experimental results

### Crystal structure of $Zn_3P_2$

$Zn_3P_2$, prepared by Stackelberg and Paulus in 1935[1], is known to be a $D5_9$-tetragonal† crystal with unit cell dimensions $a=8.113$Å and $c=11.47$Å. The space gruop is $P4_2/nmc$. They suggested similar $D5_9$-tetragonal unit cells $a=8.316$Å, $c=11.76$Å for $Zn_3As_2$ and $a=8.945$Å, $c=12.65$Å for $Cd_3As_2$ respectively. However, Cole *et al.*[7] postulated in 1956 a larger $D5_9$*-tetragonal‡ unit cell for $Zn_3As_2$ and

†, ‡ $D5_9$ and $D5_9$* are 'Strukturbericht' symbols.

5) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)

6) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **42**, 48 (1966)

7) A. Cole, F. W. Chambers and H. M. Dunn, *Acta Cryst.*, **9**, 685 (1956)

$Cd_3As_2$. This unit cell is related to the former $D5_9$-tetragonal structure as; $a \simeq a'\sqrt{2}$, $c=2c'$. The $D5_9$-tetragonal structure, now discredited for $Zn_3As_2$ and $Cd_3As_2$, also has been considered to be suspect for $Zn_3P_2$ and $Cd_3P_2$. According to the present investigation on $Zn_3P_2$, it was, however, confirmed that all of the observed reflections in the X-ray diffraction could be accounted for by postulating the $D5_9$-tetragonal unit cell given by Stackelberg and Paulus. Therefore, $Zn_3P_2$ and probably $Cd_3P_2$ may have a similar but a little different structure from those of $Zn_3As_2$ and $Cd_3As_2$. The data of X-ray diffraction patterns for $Zn_3P_2$ are shown in Table 1.

$Zn_3P_2$ is a black semiconductor with a metallic luster. It is easily attacked by aqueous HCl, $H_2SO_4$ and $HNO_3$. The measured density is 4.21～4.76g/cm³.

Table 1 Data of X-ray diffraction diagrams for tetragonal $Zn_3P_2$

| $d$ (Å) | $I/I_0$ | $hkl$ |
|---|---|---|
| 4.635 | 3 | 102 |
| 3.824 | 8 | 201 |
| 3.459 | 20 | 211 |
| 3.290 | 30 | 202 |
| 3.066 | 15 | 212 |
| 2.850 | 50 | 220, 004 |
| 2.759 | 30 | 203 |
| 2.632 | 18 | 213, 301 |
| 2.446 | 13 | 302 |
| 2.191 | 4 | 303 |
| 2.010 | 100 | 224, 400 |
| 1.7368 | 2 | 242 |
| 1.7160 | 10 | 206 |
| 1.6441 | 6 | 404 |

**General view of reactions in the Zn-P system under high pressure**

It was confirmed in the present work that the reaction processes in the Zn-P system under high pressure could be represented as follows:

Under pressures below 15 kb;

$$3Zn+2P \longrightarrow Zn_3P_2, \quad \text{at } 150\sim300^\circ C \tag{1}$$

$$Zn_3P_2+4P \longrightarrow 3ZnP_2 \text{ (monoclinic)}, \quad \text{at } 450^\circ C \tag{2}$$

$$ZnP_2 \text{ (monoclinic)} \longrightarrow ZnP_2 \text{ (tetragonal)}, \quad \text{at } 600^\circ C \tag{3}$$

Under pressures above 20 kb;

$$3Zn+2P \longrightarrow Zn_3P_2, \tag{1}$$

$$Zn_3P_2+4P \nearrow ZnP_2 \text{ (monoclinic)}, \tag{2}$$

$$Zn_3P_2+4P \searrow ZnP_2 \text{ (pseudo-cubic)}, \tag{4}$$

$$ZnP_2 \text{ (monoclinic)} \searrow ZnP_2 \text{ (pseudo-cubic)}, \tag{5}$$

$$ZnP_2 \text{ (tetragonal)} \nearrow$$

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$$ZnP_2 \text{ (pseudo-cubic)} + 2P \longrightarrow ZnP_4. \quad (6)$$

Below 15 kb, the reaction products are just the same as those obtained at atmospheric pressure. Independently of the composition of the starting mixtures reaction (1) proceeds first at about 150°C. In the presence of excess zinc, only $Zn_3P_2$ is formed in any experimental conditions under pressures. On the other hand, in the presence of excess phosphorus reaction (1) is followed by reaction (2) above 450°C and the monoclinic $ZnP_2$ is prepared. The monoclinic $ZnP_2$ once formed proceeds to transform into the tetragonal modification above 600°C through the reaction (3). The phase transition gives practically a 100 per cent yield of the tetragonal modification above 900°C under 15 kb.

In the pressure range above 20 kb, reaction (1) proceeds at 150°C to form $Zn_3P_2$ independently of the composition of reactants, which is the same as in the case below 15 kb. In the presence of excess zinc only $Zn_3P_2$ is formed. However, in the specimen containing excess phosphorus, both the monoclinic and the pressure-induced modifications of $ZnP_2$ are produced through reactions (2) and (4), their ratios being controlled by the experimental conditions. This high pressure modification is also prepared by the polymorphic transitions of the monoclinic and the tetragonal $ZnP_2$ (5). The pressure-induced $ZnP_2$ reacts further with excess black phosphorus to form a new crystalline $ZnP_4$ above 500°C under 40 kb (6).

In the present paper the kinetics of reaction (1) in the solid state will be described in the next section. The physical and chemical properties of new high pressure modifications of $ZnP_2$ and $ZnP_4$, and the effects of temperature and pressure on the polymorphic transitions of $ZnP_2$ will be presented in the following paper[4].

**Kinetics of the solid state reaction of zinc with phosphorus to form $Zn_3P_2$ under high pressure**

As mentioned above, it was confirmed that only $Zn_3P_2$ was formed in the Zn : P=3 : 2 starting mixture in any experimental conditions under pressure. The kinetical treatment of the solid state reaction has been carried out at temperatures of 50~400°C and pressures of 5~50 kb.

In Fig. 1 the *P–T* phase diagrams of zinc and phosphorus are given. According to Kennedy, Newton and their coworkers[8], the melting point of zinc increases with pressure almost linearly from 419°C at atmospheric pressure to about 600°C at 50 kb. As seen in the figure, metastable red phosphorus transforms into stable black phosphorus at about 500°C and 10 kb[9][10]. The transition temperature gradually decreases with pressure to about 200°C at 60 kb. According to Butuzov[11], the melting temperature of black phosphorus increases abruptly by compression from 620°C under the normal pressure to 1100°C at 20 kb. Thus, below 300°C, both zinc and phosphorus are in solid state under the pressures covered. Although $Zn_3P_2$ is known to decompose[3] gradually at about 400°C under normal pressure and so has not a definite melting point, it may be also in solid state below 300°C under pressures. Consequently the reaction of zinc with phosphorus proceeds in solid state in the lower temperature range below 300°C under pressures.

8) G. C. Kennedy and R. C. Newton, "Solids under Pressure" p. 163, ed. by W. Paul, D. M. Warschauer, McGraw-Hill, New York (1963)
9) L. J. Long, G. B. Guarise and A. Marani, *Symposium Dinamica delle Reazioni Chimiche*, Consiglio Nazionale delle Ricerche, Roma (1967) p. 97
10) G. B. Guarise, A. Marani and M. Pagannone, *Atti Ist. Veneto Sci. Lett. Arti*, **125**, 11 (1967)
11) V. P. Butuzov, *Kristallogr*, **2**, 536 (1957)

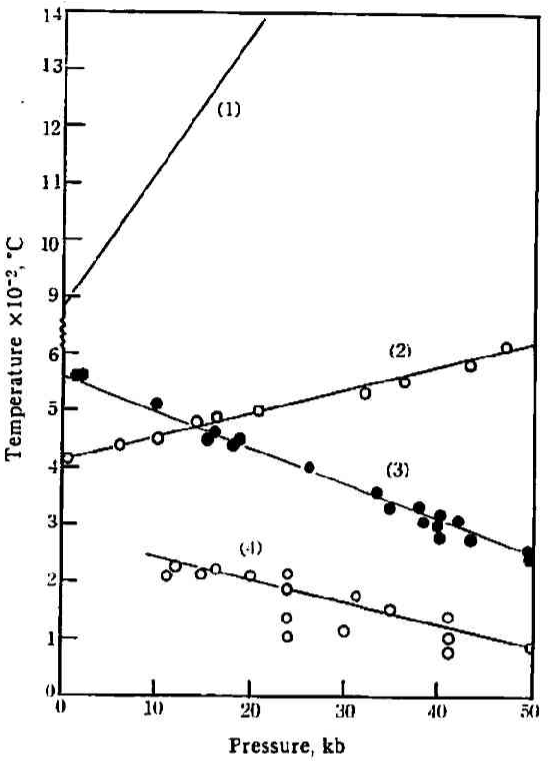


Fig. 1 *P-T* diagrams of zinc and phosphorus
(1) melting curve of black P (Butuzov)
(2) melting curve of Zn (Kennedy, Newton *et al.*)
(3) red→black transition of P (Guarise, Marani *et al.*)
(4) white→black transition of P (Pätz)

The reaction yield can be defined as follows:

$$\frac{\text{Weight of } Zn_3P_2 \text{ formed}}{\text{Total weight of the specimen}} \times 100\,(\%)\ .$$

In Fig. 2 the reaction yields in 60 minutes are plotted against the temperature for three pressures.

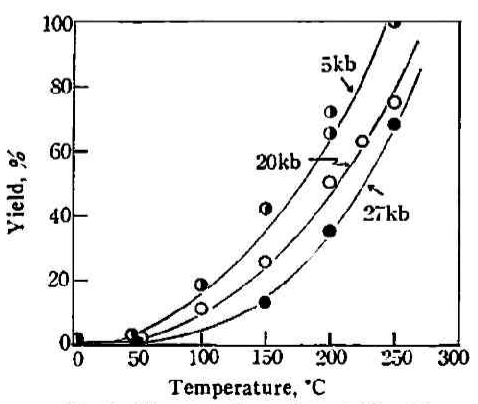


Fig. 2 Changes of reaction yields with temperature
Reaction time: 60 minutes

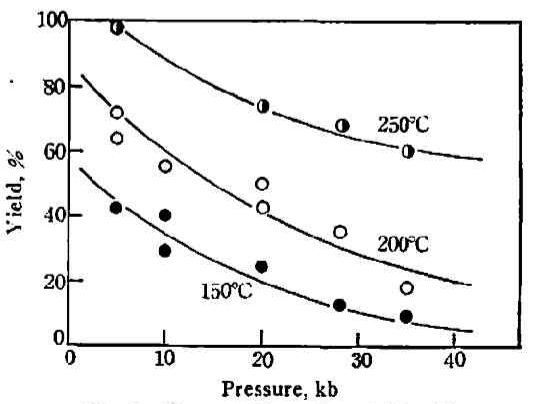


Fig. 3 Changes of reaction yields with pressure
Reaction time : 60 minutes

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The reaction proceeds at about 100°C. The reaction yields increase with temperature and decrease by compression. The plots of reaction yields *versus* pressure are given in Fig. 3 for three temperatures. The reaction yields decrease almost linearly with pressure at any temperature. The effect of pressure is more remarked below 200°C.

The reaction yields *versus* time are shown in Figs. 4 (a), (b) and (c) for various experimental conditions. Above 300°C the reaction are brought to completion within 30 minutes below 10 kb. The reaction proceeds mainly within first 60 minutes below 250°C and after then the reaction yield is kept almost constant within the experimental errors.

The general factors governing the kinetic laws for solid-solid reactions are as follows:

1) The rates of transfer of materials between phases and chemical reactions at phase boundaries
2) The rates of diffusion of reactants
3) The rates of nucleation and recrystallization

The form of the overall kinetic law will depend on the relative rates of these processes. Frequently one process will be rate-controlling.

In the solid state reaction of zinc with phosphorus under pressures, the rates of diffusion of the reactants through each other and through the products may be the rate-controlling in view of the facts that pressure retards the reaction and the reaction yield *versus* time plots give a parabolic curve. For this reaction, the change of molecular volume $\Delta V$ is calculated to be about $+1.18\,cm^3$/mole crystallo-

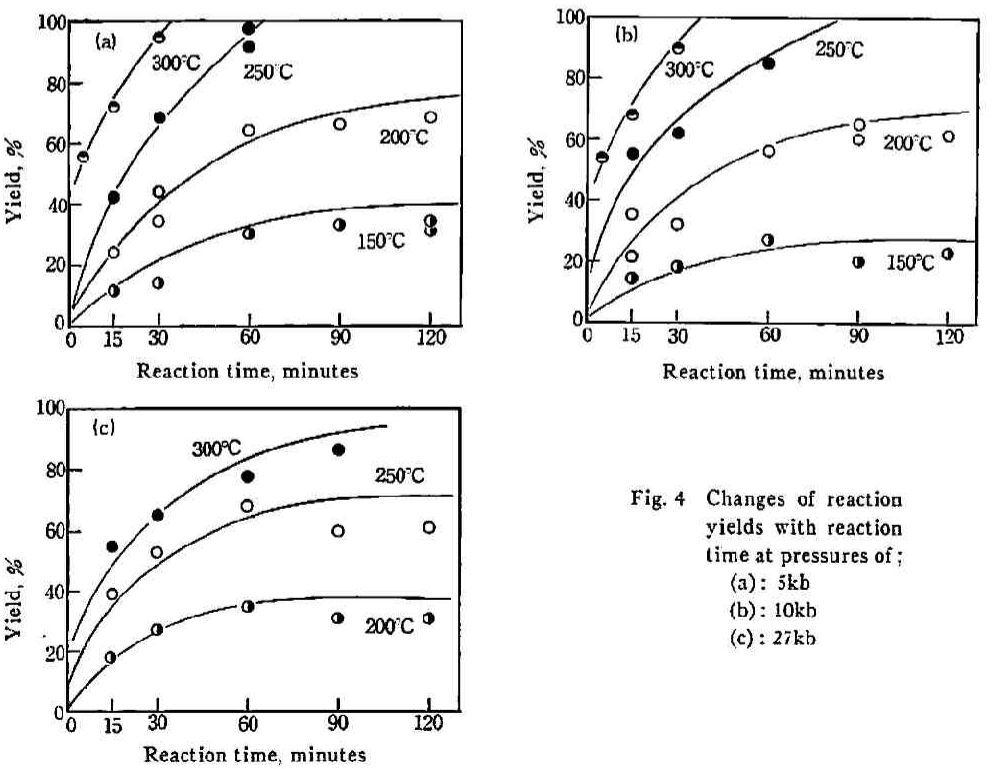


Fig. 4 Changes of reaction yields with reaction time at pressures of;
(a): 5kb
(b): 10kb
(c): 27kb

graphically. Therefore the diffusion of reactants into $Zn_3P_2$ may be especially important because the transfer of the reactants through the microcracks of the particles becomes more and more difficult with the formation of $Zn_3P_2$.

The formal statement of any kinetic law will also depend upon the geometry of the reacting phases and the spatial and temporal sequence in which various phases appear. Jander[12] gave a mathematical treatment of diffusion-controlled solid state reaction, assuming that a very small spherical component 1, which exists much more abundantly than component 2, diffuses through a concentric shell of product on the outside of the larger spherical component 2. However, his treatment is only an approximation to the reaction between the spherical particles because it is assumed that the diffusion surface is always kept constant.

Serin and Ellickson[13] published a more rigorous diffusion-controlled rate equation originating in Wagner's[14] equation for solid-vapor reactions. Mason[15] has also derived this equation and subjected it to the experimental test with very good results. On the assumption that diffusion occurs in or out of homogeneous spherical particles of radius $a$, the rate law may be derived from Fick's first and second laws and expansion through a Fourier series as follows[13)15]:

$$1-x=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2Dt}{a^2}\right).$$

where $x$=fraction of reaction or diffusion that has occurred after time $t$
$a$=radius of spherical particles
$D$=diffusivity
$n$=integer equalling no. of term in the series expansion

The derivation implicitly assumes that diffusion will occur with an average diffusivity $D$ through any matrix of phases within the grain. This is, however, an approximation and averages diffusion through crystals, along their surfaces and through microcracks.

Using this equation, $x$ is determined experimentally and the corresponding value of $kt$ is calculated uniquely. It is, however, difficult to calculate $kt$ for each value of $x$ obtained since $kt$ can not be expressed as a function of $x$ in terms of any simple functions. Serin and Ellickson[13] gave a plot of $x$ *versus* $kt$ by calculating the values of $x$ for various $kt$ in advance. Thus, if one takes an experimentally determined value of $x$, the corresponding value of $kt$ can be read from the plot. The same method was applied to the data obtained in the present work.

Figs. 5 (a), (b) and (c) present the plots of $kt$ *versus* $t$ for pressures of 5, 10 and 27 kb respectively. It is observed in Fig. 5(a) that the values of $kt$ increase approximately linearly with time at 250°C. On the other hand, other two curves give straight lines after the initial part of the reaction as shown by the dotted lines. The initial part of the reaction is also nearly a straight line. The fact that the curve can be divided into two straight lines with different slopes suggests that the reaction proceeds in two stages.

12) W. Jander, *Z. anorg. Chem.*, **163**, 1 (1927); **166**, 31 (1927); **166**, 33 (1927)
13) B. Serin and R. T. Ellickson, *J. Chem. Phys.*, 9, 742 (1941)
14) H. Dünwald and C. Wagner, *Z. physik. Chem.*, **B24**, 53 (1934)
15) H. F. Mason, *J. Phys. Chem.*, **61**, 796 (1957); W. P. Riemen and F. Daniels, *ibid.*, **61**, 802 (1957)

The same trend can be seen also in Figs. 5(b) and (c). The former stage may be principally surface reaction (and surface diffusion). The later one, after the initial stage of the reaction is completed, is controlled by the diffusion into the interior of the solids. The surface reaction occurs first and is a fast reaction which is completed in a short time. After the surface is covered and the surface reaction is

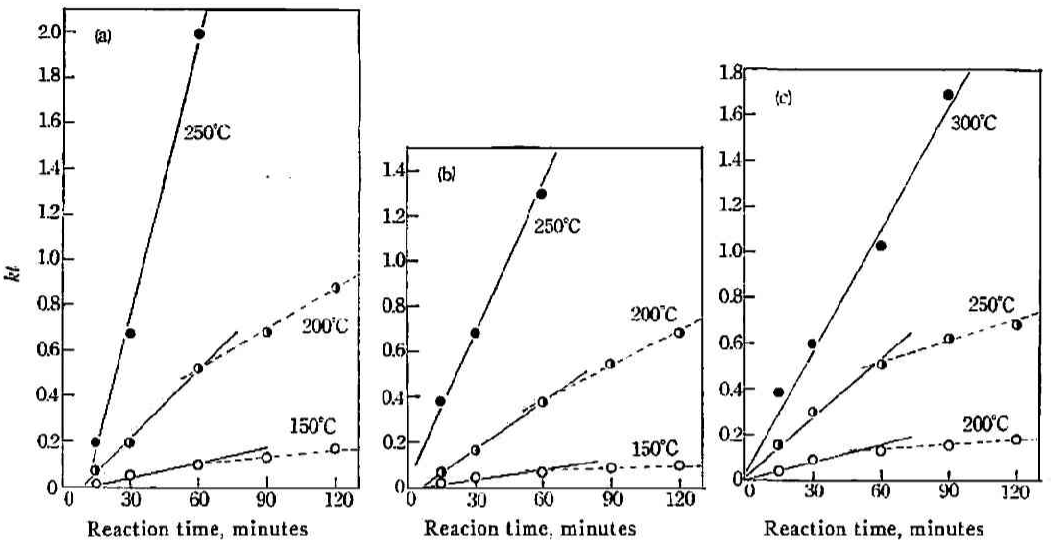


Fig. 5 Rate constant $k$ multiplied by time *versus* time. (a): 5 kb, (b): 10 kb, (c): 27 kb

completed, the dominant mechanism is a volume diffusion. The stress in the reactants would also accelerate the initial reaction.

The slope of the line gives the value of the rate constant $k$ for the solid state reaction controlled by diffusion. The values of the rate constant calculated are summarized in Table 2. For the rate equation of the diffusion given earlier the surface reaction (and the surface diffusion) were not taken into consideration, but it was also used for convenience to calculate the initial rate constant.

The diffusivity $D$ is related to the rate constant $k$ by the equation $k=\pi^2 D/a^2$. On the assumption that $Zn_3P_2$ has an average particle radius of 5 $\mu$ similarly to zinc and phosphorus, $D$ is calculated to be of the order $10^{-11}\sim10^{-13}$ cm$^2$/sec for the volume diffusion.

Table 2 Kinetic data for the reaction $3Zn+2P\rightarrow Zn_3P_2$ in the solid state under high pressures

| Pressure (kb) | Temperature (°C) | Initial rate const. (min$^{-1}$) | Rate const. (min$^{-1}$) | Diffusivity (cm$^2$/sec) |
|---|---|---|---|---|
| 5 | 150 | $1.50\times10^{-3}$ | $1.17\times10^{-3}$ | $4.95\times10^{-13}$ |
| 5 | 200 | $7.66\times10^{-3}$ | $5.83\times10^{-3}$ | $2.46\times10^{-12}$ |
| 5 | 250 | $3.49\times10^{-2}$ | $3.49\times10^{-2}$ | $1.48\times10^{-11}$ |
| 10 | 150 | $1.00\times10^{-3}$ | $6.67\times10^{-4}$ | $2.82\times10^{-13}$ |
| 10 | 200 | $5.91\times10^{-3}$ | $5.17\times10^{-3}$ | $2.18\times10^{-12}$ |
| 10 | 250 | $2.24\times10^{-2}$ | $2.24\times10^{-2}$ | $9.48\times10^{-12}$ |
| 27 | 200 | $1.75\times10^{-3}$ | $8.33\times10^{-4}$ | $3.52\times10^{-13}$ |
| 27 | 250 | $6.34\times10^{-3}$ | $3.67\times10^{-3}$ | $1.55\times10^{-12}$ |
| 27 | 300 | $1.91\times10^{-2}$ | $1.91\times10^{-2}$ | $8.08\times10^{-12}$ |

In Fig. 6 the plots of $\log k$ *versus* reciprocal of the absolute temperature are given. The apparent activation energy $E$ for the diffusion process can be estimated from the slope of the line by the following relation:

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = \frac{E}{RT^2},$$

where $k$ is the rate constant, $T$ the absolute temperature, $P$ the pressure and $R$ the gas constant. The solid lines in the figure correspond to the initial stage of the reaction and the dotted lines to the following stages respectively.

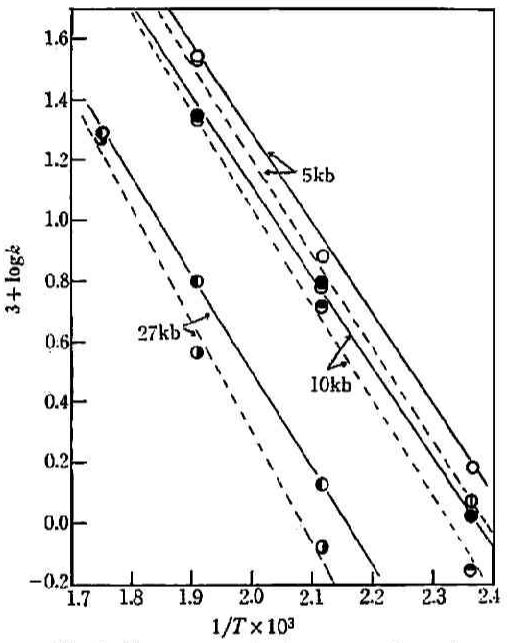


Fig. 6 Log rate constant *versus* reciprocal of absolute temperature

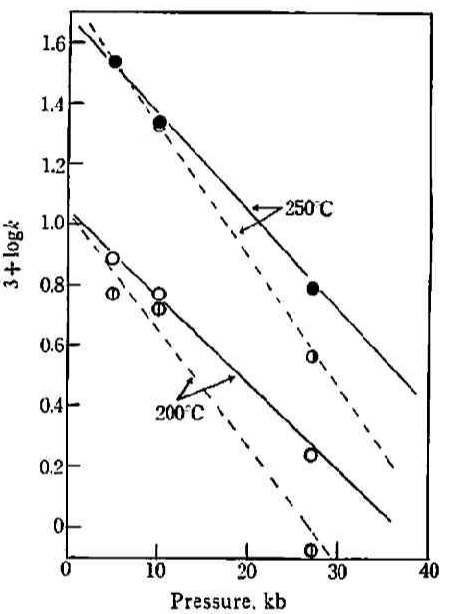


Fig. 7 Log rate constant *versus* pressure

In Fig. 7 $\log k$ are plotted against pressure for 200 and 250°C. The activation volume $\Delta V^{\ddagger}$ in the diffusion process can be estimated from the slope of the line by the following relation:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT}.$$

The results are listed in the following table.

Table 3 Apparent activation energies and activation volumes for the reaction $3Zn+2P \rightarrow Zn_3P_2$ in the solid state under high pressures

| | Activation energy | | | Activation volume | |
|---|---|---|---|---|---|
| Pressure (kb) | Surface reaction (and diffusion) $E$ (kcal/mole) | Volume diffusion $E$ (kcal/mole) | Temperature (°C) | Surface reaction (and diffusion) $\Delta V^{\ddagger}$ (cm³/mole) | Volume diffusion $\Delta V^{\ddagger}$ (cm³/mole) |
| 5 | 13.0 | 14.2 | 200 | 2.6 | 3.3 |
| 10 | 13.3 | 14.9 | 250 | 3.6 | 4.1 |
| 27 | 15.0 | 17.5 | | | |

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Although the mathematical form of the rate equation for a reaction in a mixture of powders may be considerably different from its form for the same reaction between the two parallel slabs of the reactants, the fundamental is the same in both cases. The rates of solid state reactions are generally governed by the rate of diffusion of one of the reactants. The reaction between the two parallel slabs of zinc and red phosphorus was undertaken in order to make clear which component is more diffusive under high pressure, at 300°C under 5 kb, using a piece of platinum foil as a marker. In this experiment $Zn_3P_2$ was confirmed on the phosphorus side but not on the zinc side. Therefore, it is evident that zinc being more diffusive, diffuses more easily into $Zn_3P_2$ as compared with phosphorus.

At atmospheric pressure the self-diffusion coefficients of single crystal of zinc are known to be approximately of the order of $10^{-11}$ cm$^2$/sec at 260°C and $10^{-9}$ cm$^2$/sec at 390°C[16]. The diffusion coefficients of zinc into Al or Cu are $10^{-10}\sim10^{-12}$ cm$^2$/sec at 400°C[16]. According to Liu and Drickamer[17], the self-diffusion coefficient of zinc is reduced to be of the order $10^{-10}\sim10^{-11}$ cm$^2$/sec by pressure of 10 kb. Although there are few measurements on phosphorus, the diffusivity of phosphorus into silicon[18] is known to be $10^{-12}\sim10^{-13}$ cm$^2$/sec even at 1,200°C at atmospheric pressure. The diffusion coefficients of antimony and bismuth[18], which are the elements in the same group V as phosphorus, are also known to be of the orders of $10^{-13}\sim10^{-14}$ cm$^2$/sec at 1,200°C and $10^{-16}$ cm$^2$/sec at 250°C respectively. The diffusivities for these non-metallic elements are considerably small as compared with those of typical metallic elements. From the fact that in the present work the diffusion coefficients $10^{-12}\sim10^{-14}$ cm$^2$/sec were obtained in the lower temperature range below 250°C under pressures of 5~30 kb, zinc may be the more diffusive element in the Zn-P system. This estimation is not inconsistent with the result obtained in the reaction between the two parallel slabs of zinc and phosphorus.

According to Liu and Drickamer[17], the activation enthalpy $\Delta H^{\ddagger}$ for the self-diffusion of zinc is 16~25 kcal/g-atom and the apparent activation volumes at 307°C under 10 kb are 3.62 and 2.68 cm$^3$/g-atom for the directions parallel and perpendicular to the *c*-axis respectively. Although the activation enthalpy is not rigorously equal to the apparent activation energy, the activation energy 14~18 kcal/mole for the volume diffusion obtained in the present work is quite near to the activation enthalpy for the self-diffusion of zinc. The activation volume 3.3~4.1 cm$^3$/mole is also in good agreement with the activation volume for self-diffusion of zinc. Thus, the kinetic data are explained on the hypothesis that the rate of reaction may be determined by the diffusion of zinc followed by a slower diffusion of phosphorus.

## Considerations

At atmospheric pressure zinc phosphide $Zn_3P_2$ is usually prepared by the heterogeneous liquid-vapor reaction of molten zinc and phosphorus vapor in an evacuated silica tube. The major difficulties in preparing zinc phosphide arise from the fact that it has not a definite melting temperature but decomposes at about 400°C under reduced pressure. It is not possible to overcome this difficulty by

16) W. Jost, "Diffusion in Solids, Liquids and Gases", Academic Press, Inc. New York, (1952)
17) T. Liu and H. G. Drickamer, *J. Chem. Phys.*, **22**, 312 (1954)
18) M. F. Millea, *J. Phys. Chem. Solids*, **27**, 315 (1966)

phosphorus.
maintaining a constant pressure of excess phosphorus in a sealed ampoule.

The reaction between the molten zinc and the phosphorus vapor occurs at about 500°C but the zinc phosphide forms a layer on the zinc surface preventing more phosphorus from reacting with zinc. Therefore, a quantitative reaction between the elements is never obtained at atmospheric pressure.

On the other hand, high pressure prevents the sublimation and the decomposition of products and increases the available temperature range for the reactions. It is therefore very useful to apply high pressure to the reactions between two elements, one of which has comparatively low reactivity and high melting temperature and the other is very volatile at the required temperatures. If there is an overall volume change related with the reaction and the reaction process is the rate determining step, the application of pressure may also serve to speed up or slow down certain reactions whose rates at ordinary pressure are too low or too high to be conveniently studied and sometimes it may radically change the courses of the reactions.

The reactions of boron with phosphorus[19] and boron with arsenic[6] were undertaken at high temperature and high pressure previously from this standpoint.

As for the B-P system, sphalerite type BP, rhombohedral $B_{13}P_2$ and other several compounds have been known. Cubic BP decomposes to $B_{13}P_2$ by releasing phosphorus at about 1,100°C under reduced pressure. At high pressures, it was confirmed that only cubic BP is formed throughout the experimental conditions of 600～1,400°C and 9～15 kb independently of stoichiometric composition of starting mixtures. It may be attributed to the fact that the cubic form is the most stable one at high pressures. The lattice constant 4.538Å is in good agreement with the results of Perri *et al.*[20] and Williams *et al.*[21] for cubic BP obtained under normal conditions. BP has high hardness and high resistivity to the mineral acids. Therefore, it can be chemically isolated from unreacting boron and phosphorus by treating it with heated, concentrated nitric acid.

Although the reaction of boron with arsenic is one of the examples of very slow reaction under atmospheric conditions[20)~22)], it is also much accelerated by pressure[6]. The reaction completes within 10～15 minutes at 1,200°C under 15 kb. At pressures of 2～33 kb, arsenic in the starting mixture is completely consumed to form cubic BAs at first at about 1,150°C and then BAs reacts further with excess boron at 1,250°C as follows:

$$2BAs + 11B \longrightarrow B_{13}As_2.$$

Under atmospheric pressure BAs has not a definite melting temperature but it decomposes to the rhombohedral $B_{13}As_2$ at about 1,100°C, releasing arsenic. When unreacting boron and arsenic and $B_{13}As_2$ coexist with cubic BAs, the isolation of BAs by the chemical method is not easy to make since BAs is more changeable than boron and $B_{13}As_2$ in the chemical treatments. The zone melting method is also useless because of the high temperature decomposition of BAs. On the other hand, boron reacts completely with arsenic to prepare BAs at about 1,200°C under 4～5 kb by use of the starting mixture of

19) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **40**, 105 (1964)
20) J. A. Perri, S. LaPlaca and B. Post, *Acta Cryst.*, **11**, 310 (1958)
21) F. V. Williams and R. A. Ruehrwein, *J. Am. Chem. Soc.*, **82**, 1330 (1960)
22) S. M. Ku, *J. Electrochem. Soc.*, **113**, 813 (1966)

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B : As=1 : 2~2.5, while $B_{13}As_2$ is not prepared at all in this condition. Therefore, BAs can be isolated from unreacting arsenic by being oxidized with dilute nitric acid[23]. Thus, it is to be noted that both suppression of side reactions and the prevention of the decomposition of products are often useful to obtain pure objects.

The reaction in which only a stable compound with a simple stoichiometric composition is formed throughout the experimental conditions is quite suitable to study chemical kinetics. In the study of chemical kinetics of reactions, it is meaningful to use the pressure as an experimental parameter which may be varied at will like the temperature. Thus the effect of pressure on the rate of reaction was investigated quantitatively on the reaction of boron with phosphorus to form the cubic sphalerite type BP[19]. In the lower temperature range below 1,100°C, the reaction is retarded by pressure. On the other hand, the reaction is accelerated with the increase of pressure above 1,200°C and completes within one hour at 1,300°C under 15 kb. The effect of pressure on the reaction reverses at about 1,100°C. It would arise mainly from the change of the reaction mechanism caused by the solid-liquid transition of phosphorus or boron phosphide with temperature. The decrease of the reaction yield with pressure would be ascribed to the suppression of diffusion or the migration of materials by pressure and this process would determine the reaction rate. On the contrary, the process of reaction of boron with phosphorus would be the rate determining above 1,200°C.

Kinetic analysis of the experimental data performed on the basis of the first-order rate equation gives the values of the apparent activation energy and the apparent activation volume as shown in Table 4.

Table 4 Apparent activation energies and activation volumes for the reaction B+P→BP under high pressure

| Temperature, °C | Activation energy, kcal/mole | Activation volume, $cm^3$/mole |
|---|---|---|
| below 1,250 | 47.8 | −3.7 |
| above 1,250 | 38.2 | −4.1 |

The differences between the values below and above 1,250°C would depend on the initial state of phase of phosphorus, solid or liquid.

As mentioned above, it is interesting physico-chemically to make clear the difference of the reaction kinetics above and below the liquid-solid transition temperature of reactants and/or products. However it is usually very difficult to measure the different reaction rates by the same method in the solid-solid and the liquid-solid reactions. Generally the reactions with convenient rate to be studied in the solid state have too high rate in the temperature range above the melting temperature of one of the component elements as seen in the reactions of boron with arsenic[6] and zinc with phosphorus under high pressure. The reaction of zinc with phosphorus completes almost instantly when the temperature reaches the melting temperature of zinc.

On the contrary, the very slow reactions which have measurable rate only above the melting temperature have often too slow rate in the solid state. Therefore, it is desirable to prepare two different

23) J. Osugi, K. Shimizu, Y. Tanaka and K. Kadono, *This Journal*, **36**, 54 (1966)

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methods of measurement at least for this purpose.

In the solid-state reactions involving the changes in chemical composition, one reactant at least diffuses into the other components in order that the reaction may propagate. For this reason, the concepts involving "concentrations" and "mechanisms derived from an apparent experimental order of reaction" are often of little intrinsic significance. Thus discussion of mechanism involves the rate of movement of the interface boundary. The mathematical formulation of the rate process must be expressed in terms of both spatial and time co-ordinates. Even if an activation energy and an activation volume are obtained validly, their identification with a rate process will rely on a suitable hypothesis for the mechanism of the reaction. Therefore, they may refer to the diffusion process, to the chemical reaction process or a set of coupled processes.

In the solid state reactions under high pressure, it should be also noted that the reactions generally set out at considerably lower temperatures than the melting temperatures of component elements since pressure makes the distances between atoms much shorter as compared with those at normal pressure. The reaction of zinc with phosphorus under high pressure, for example, sets out at about 100°C which corresponds approximately to 25 per cent of the melting temperature of zinc. A similar phenomenon is observed in the reaction of silicon with carbon to form $\beta$-SiC at high pressure. The reaction sets out at about 800°C under 10~30 kb. In this condition both silicon and carbon are just in the solid state.

As stated in the boron-phosphorus system[19], the stress in the reactants would also accelerate the initial reaction. This effect, together with the difficulty of manipulation under high pressure, makes the kinetic analysis of experimental data rather complicate.

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